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Letter to Editor

COMPARATIVE ANALYSES OF THERMODYNAMIC PROPERTIES ASSESSMENTS, PERFORMED BY GEOMETRIC MODELS: APPLICATION TO THE Ni–Bi–ZN SYSTEM

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Abstract

The thermochemical properties of metals and alloys are essential for the chemists to invent and improve metallurgical and materials' design processes. However, the properties of multicomponent systems are still scarcely known due to experimental difficulties and the large number of related systems. Thus, the modelling of some thermodynamic properties would be advantageous when experimental data are missing.

Considering mentioned facts, geometric models to estimate some thermodynamic properties for the liquid phase of the Ni–Bi–Zn systems. The calculations have been performed in a wide temperature range (1000–2000 K). Ternary interaction parameters for the liquid phase allowing molar Gibbs excess energy calculation have been determined.

Keywords: thermodynamics, general solution model, ternary interaction parameters, Bi-Ni-Zn, ternary system

1. Introduction

The elements constituting the system Bi–Ni–Zn are among those belonging to a variety of potential lead-free solder materials. The latter are expected to be designed on the bases of systems including low-melting elements like Bi alloyed with Zn or/and Sn. On the other side, nickel metallization often appears as part of the electronics assembling and numerous investigations of such Ni-containing systems are reported [1–15].

The binary end-systems Bi–Ni, Bi–Zn and Ni–Zn are relatively well studied and reliable optimizations have been compiled in the thermodynamic database SOLDERS [16], resulting from the European concerted action COST 531. These descriptions are used in the present work for the purpose to derive the excess Gibbs energy of the ternary Bi–Ni–Zn liquid phase.

2. Theoretical basis

Binary end-systems: The binary end-systems (Bi–Ni, Bi–Zn, Ni–Zn) are reproduced in Figs. 1–3, respectively, in order to remind some general notions about their construction.

Assessments basis: The assessments are done by means of the most common classic geometric models of Kohler [20], Muggianu [21], Toop [22] and Hilert

[23], as well as by means of the newly-developed but prominent general solution model (GSM) introduced by Chou [24, 25].



Figure 1. Ni–Bi phase diagram calculated with parameters optimized by Vassilev et al. [10, 12, 16].

The excess Gibbs energy (ΔG^E , J/mol) of the ternary liquid phase are chosen as a function whose values had to be calculated by various models and compared. This quantity describes the contribution of the non-ideal mixing to the thermodynamic properties of a solution phase. The excess Gibbs energies (at specific compositions) of every binary end-system are

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Figure 2. Bi–Zn phase diagram calculated with adjustable coefficients of Malakhov [16, 17].



Figure 3. Ni–Zn phase diagram calculated with adjustable coefficients of Vassilev et al. [16, 19]

needed as departure points. They are calculated by means of Thermocalc software [18] by using optimized parameters recently selected as result of the European concerted action for development of lead-free solders COST 531 [16]. Thus, in the general case, a ternary system with constituents 1, 2 and 3 mole fractions of the respective components x_1 , x_2 and x_3 is considered.

According to GSM model, the composition dependence of the binary Gibbs molar excess energies is given by the expression:

$$\Delta G_{ij}^{E} = X_{i}X_{j}(A_{ij}^{0} + A_{ij}^{1}(X_{i} - X_{j}) + A_{ij}^{2}(X_{i} - X_{j})^{2} + \dots + A_{ij}^{n}(X_{i} - X_{j})^{n})$$
(1)

where, A^{o}_{ij} , A^{1}_{ij} , A^{2}_{ij} are adjustable temperature dependent parameters (related to the Redlich-Kister formalism [27]) belonging to the binary system "ij"; X_i and X_j indicate the mole fractions of the corresponding constituents.

The Gibbs molar excess energy of a ternary phase is assessed by means of the expression:

$$\Delta G^{E} = X_{1}X_{2}\Delta G^{E}_{12} + X_{2}X_{3}\Delta G^{E}_{23} + X_{3}X_{1}\Delta G^{E}_{31} + \Delta G^{E}_{123}$$
(2)

where ΔG^{E}_{123} is the contribution of the ternary non-ideal mixing, which can be calculated by eq. (6):

$$\Delta G_{123}^{E} = X_{1} X_{2} X_{3} f_{123} \tag{3}$$

 f_{123} is a ternary interaction coefficient related to the Redlich-Kister ternary interaction parameter.

The GSM [24, 25] allows to calculate this parameter, using the optimized values A^{o}_{ij} , A^{1}_{ij} , A^{2}_{ij} as follows:

$$f_{123} = (2\xi_{12} - 1)\{A_{12}^{2}((2\xi_{12} - 1)X_{3} + 2(X_{1} - X_{2})) + A_{12}^{1}\} + (2\xi_{23} - 1)\{A_{23}^{2}((2\xi_{23} - 1)X_{1} + 2(X_{2} - X_{3})) + A_{23}^{1}\} + (2\xi_{31} - 1)\{A_{31}^{2}((2\xi_{31} - 1)X_{2} + 2(X_{3} - X_{1})) + A_{31}^{1}\}$$
(4)

where x_{ij} are called "similarity coefficients", defined by h_i - called "deviation sum of squares":

$$\xi_{ij} = \eta_i / (\eta_i + \eta_j)$$
⁽⁵⁾

According to GSM the values of h_i are functions of ΔG^{E}_{ij} , and are easily calculated when the adjustable coefficients of the three binary end-systems are known.

$$\Delta G_{123}^{E} = x_1 x_2 (A_{12}^{0} + A_{12}^{1} (x_1 - x_2) + A_{12}^{2} (x_1 - x_2)^2) + x_2 x_3 (A_{23}^{0} + A_{23}^{1} (x_2 - x_3) + A_{23}^{2} (x_2 - x_3)^2) + (6) + x_3 x_1 (A_{31}^{0} + A_{31}^{1} (x_3 - x_1) + A_{31}^{2} (x_3 - x_1)^2) + f_{x_1 x_2 x_3}$$

Molar excess Gibbs energy of the liquid phase $(\Delta G^{E}_{_{NiBiZn}})$ is calculated by means of Eqs. (1–6).

In this work, values of the ternary integral Gibbs excess energies ($\Delta G^{ex,Liq}$, J/mol) Ni–Bi–Zn alloys, with nickel molar fractions equal to 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1, were calculated along sections with Bi/Zn molar ratio equal to 1/3, 1/1 and 3/1. The calculations are done in the temperature interval from 1000 to 2000 K.

Basic thermodynamic information of the constitutive subsystems, needed for the assessment, was taken from Ref. [10, 12, 16, 17, 19]. The optimized Redlich-Kister parameters of each system used for the assessments are compiled in Table 1.

2. Results and Discussion

Thermodynamic assessments of the liquid phase of Ni–Bi–Zn system are performed by models of Kohler [20], Muggianu [21], Toop [22], Hillert [23], Chou [24, 25] and with Thermocalc [18] using SOLDERS thermodynamic database. The latter approach takes into account simultaneously phase

System ij	Ni – Bi	Bi – Zn	Ni – Zn
Parameters	[1-2]	[2-3]	[3–1]
$A^{o}_{ij}(T)$	-6438+13.2882*T	+18265.09-8.67630*T	-50721.64+7.34178*T
$A^{1}_{ij}(T)$	-11315-1.4571*T	-6061.21+0.79581*T	+8436.3+1.97211*T
A ² _{ij} (T)	0	-6422.6+11.71966*T	-25136.08+11.79072*T
$A_{ij}^{3}(T)$		+7227.44-9.29050*T	
$A^4_{ij}(T)$		+21123.07-27.14705*T	
$A_{ij}^{5}(T)$		-20747.56+22.01759*T	
A ⁶ _{ij} (T)		-7600.36+13.15957*T	

Table 1. Ni–Bi, Bi–Zn and Ni–Zn systems liquid binary phases Redlich-Kister parameters (A°_{ij}) used for the calculation of the molar excess Gibbs energies. T – temperature, K [16].

diagrams data and the thermodynamic properties of the respective phases.

The geometric models [20–23] lead to direct assessment of $\Delta G^{ex,Liq}$, J/mol, while the GSM [24, 25] allows the calculation of ternary interactions parameters, A_{iik} (Table 2).

Comparative reviews of the molar Gibbs excess energies ($\Delta G^{ex,Liq}$) assessed at 1800 K by using geometric models and by the CALPHAD method (SOLDERS thermodynamic database, [16]) are shown in Fig. 4a-c). As one can see, in Figs. 4a and 4b, most of the assessments (curves 1, 3–5) predict (in general) negative $\Delta G^{ex,Liq}$ with a minimum in the composition interval of 0.35–0.4 mole fractions nickel. The calculations based on the GSM and the model of Muggianu (i.e. curves 2 and 6) deviate from all others predicting a minimum at around 0.6–0.7 mole fractions nickel.

It must be noted also that positive values of $\Delta G^{ex,Liq}$ in the Bi- and Zn-rich region of the liquid phase have been predicted along all three sections (Figs. 4a-c). Undoubtedly this is related to the thermochemical properties of the Bi–Zn system [5,16, 7] causing the existence of a liquid phase miscibility gap.

The molar Gibbs excess energies along the section with Bi/Zn molar ratio equal to 3/1, are positive (curves 3 and 6) or sign-changing (curves 1, 2, 4 and 5). Nevertheless, rather feeble negative values (up to -500 J/mol) have been calculated. Along this section a maximum in the composition interval of 0.7–0.8 mole fractions nickel is predicted, except by the assessment done using the GSM model (Fig.4c, curve 2). The latter is sign-changing as well but deviates symmetrically from each other calculation. The reason for this discrepancy could not be found. In Fig. 5a-c, $\Delta G^{ex,Liq}$ assessed at 1800 K have been represented as the function of the Ni, Bi and Zn content of the liquid phase, respectively. The calculations have been done by means of GSM along three (1/3, 1/1 and 3/1) fixed atomic ratios Bi/Zn, Ni/Bi and Ni/Zn, in that order. Similar approach has already been implemented in a variety of cases [27-29]. Binary molar Gibbs excess energies (calculated using SOLDERS database) in the systems Ni–Bi and Ni–Zn have been plotted as well for the sake of comparison.

In Fig. 5a-c it can be seen that $\Delta G^{ex,Liq}$ of the Ni–Zn system exhibit strong negative values. This trend is related to the solid state phase equilibria where a number of solid nickel-zinc compounds appear.

Contrary, $\Delta G^{ex,Liq}$ of Ni–Bi and Bi–Zn binary systems have positive values (Fig. 5a-c). Moreover, the Bi–Zn system (Fig. 2) has a liquid phase miscibility gap at lower temperatures. Thus the chemical interactions between Bi and Zn atoms lead to positive deviations from the ideal solutions behavior in Bi plus Zn rich regions of the ternary liquid phase. Respectively, negative $\Delta G^{ex,Liq}$, characteristic for the binary Ni–Zn liquid phase give rise to negative deviations from the ideal solutions behavior in nickel-zinc rich areas. In such a way the sign-changing $\Delta G^{ex,Liq}$ values, predicted by other geometrical methods (Fig. 4a-c) could be reasonably explained as well.

Temperature and composition $\Delta G^{ex,Liq}$ dependencies, calculated along the selected sections by means of GSM [23, 24], are exhibited in Fig. 6a-c in order to illustrate thermochemical properties of the Ni–Bi–Zn liquid phase additionally. These figures give a graphical view of the surfaces constituted by the values of the liquid phase molar Gibbs excess

Table 2. Ternary interaction parameters, A^{v}_{ijk} for the Bi–Ni–Zn liquid phase, obtained in this work with GSM, T – temperature, K.

A° _{ijk} (T) J/mol	$A^{1}_{ijk}(T) J/mol$	A ² _{ijk} (T) J/mol
-50124.1+356.331*T-42.873*TlnT	91648.53-529.465*T+63.079*TlnT	-22241.8+165.059*T-19.21*TlnT





energies. Typically, there are maximums (positive $\Delta G^{ex,Liq}$ values) in the Bi–rich regions (especially in Bi–Ni rich solutions). From the other side relatively



Figure 5. Dependence of $\Delta G^{ex,Liq}$, J/mol, assessed at 1800 K by means of GSM [24, 25], on the Ni mole fraction (a), Bi mole fraction (b) and Zn mole fraction (c). The curves denoted as $G^{ex}_{1,p}$, $G^{ex}_{1,l}$ and $G^{ex}_{3,l}$ show $\Delta G^{ex,Liq}$ values along the sections with different molar ratio equal to 1/3, 1/1 and 3/1, respectively. The G^{ex}_{1j} curves representing the respective binary molar Gibbs excess energies of adequate subsystems were calculated by using optimized parameters [15].

large negative $\Delta G^{ex,Liq}$ values are predicted for the Ni–Zn rich compositions.



Figure 6. Integral ternary molar Gibbs excess energies $(\Delta G^{ex,Liq} \text{ in J/mol})$ calculated in the temperature range 1000–2000 K along a section with Bi/Zn ratio equal to 1/1(a), 1/3 (b) and 3/1 (c)

Conclusions

Applications of the general solution model and other classical geometrical methods to predict the integral ternary molar Gibbs excess energies of the liquid phase of the Ni–Bi–Zn system have been done. The calculations have been done in the temperature interval of 1000 to 2000 K. Sign variations (i.e. positive and negative values) of the integral ternary molar Gibbs excess energies are predicted by the geometrical models, as well by CALPHAD assessment based on the optimized binary thermodynamic parameters.

The values of the ternary liquid phase molar Gibbs excess energies calculated by GSM have been compared to other models. Good agreement is was found indicating that such an approach is possible in systems where no experimental data are available.

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